Phonons in Si_{24} at simultaneously elevated temperature and pressure – Supplemental material

Xiao Tong,* Xiaolin Xu,† and B. Fultz‡
Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA

Haidong Zhang§ and Timothy A. Strobel¶
Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

Duck Young Kim**
Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA and Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China

PHONON FREQUENCY SHIFTS

Phonon frequency shifts induced by temperature alone or pressure alone are traditional topics in materials physics. There are far fewer studies on phonon frequencies at simultaneous temperature and pressure, so we offer the following framework for such work. In doing so, we have chosen to use volume rather than pressure because it is more fundamental – the positions of nuclei set the electronic energies from which the forces and pressure emerge. Here are the details for the generalized model of phonon frequency shifts presented in the main text[2].

The frequency variation $\Delta\omega$ is first linearly expanded with respect to ΔT and ΔV as

$$\Delta\omega = \left(\frac{\partial\omega}{\partial T}\right)_V \Delta T + \left(\frac{\partial\omega}{\partial V}\right)_T \Delta V \,, \tag{1}$$

where the terms can be rewritten with two material parameters: a Güneisen parameter γ and an anharmonicity parameter A[1],

$$\gamma \equiv -\frac{V}{\omega}\left(\frac{\partial\omega}{\partial V}\right)_T \,,\; A \equiv \frac{1}{\omega}\left(\frac{\partial\omega}{\partial T}\right)_V \,. \tag{2}$$

Because we want to work over a wide range of ΔT and ΔV, we also take their first-order derivatives with respect to T and P

$$g_V \equiv \left(\frac{\partial\gamma}{\partial T}\right)_V \,,\; g_T \equiv V\left(\frac{\partial\gamma}{\partial V}\right)_T \,,\; a_T \equiv V\left(\frac{\partial A}{\partial V}\right)_T \,. \tag{3}$$

We intentionally ignore the term $\partial A/\partial T$ because it is outside the realm of many body theory for phonon-phonon anharmonicity[3]. Using Eq. 2 with A_0 and γ_0 as parameters for small ΔV and ΔT

$$\begin{aligned}\left(\frac{\partial\omega}{\partial T}\right)_V \Delta T &= \omega\left[A_0 + \frac{1}{2}\left(\frac{\partial A}{\partial V}\right)_T \Delta V\right]\Delta T \\ &= \omega\left[A_0 + \frac{a_T}{2}\left(\frac{\Delta V}{V}\right)\right]\Delta T \end{aligned} \tag{4}$$

$$\begin{aligned}\left(\frac{\partial\omega}{\partial V}\right)_T \Delta V &= -\omega\left[\gamma_0 + \frac{1}{2}\left(\frac{\partial\gamma}{\partial T}\right)_V \Delta T + \frac{V}{2}\left(\frac{\partial\gamma}{\partial V}\right)_T \left(\frac{\Delta V}{V}\right)\right]\frac{\Delta V}{V} \\ &= -\omega\left[\gamma_0 + \frac{g_V}{2}\Delta T + \frac{g_T}{2}\left(\frac{\Delta V}{V}\right)\right]\frac{\Delta V}{V} \,, \end{aligned} \tag{5}$$

where a factor of $1/2$ is used with the second-order terms to obtain their average contributions to frequency shifts.

Substituting Eq. 4 - 5 into Eq. 1 gives the fractional frequency shift

$$\begin{aligned}\frac{\Delta\omega}{\omega} &= A_0\Delta T - \gamma_0\frac{\Delta V}{V} \\ &\quad + \frac{1}{2}\left[-g_V\Delta T + a_T\Delta T - g_T\left(\frac{\Delta V}{V}\right)\right]\frac{\Delta V}{V} \,. \end{aligned} \tag{6}$$

The fractional volume change can be approximated as

$$\frac{\Delta V}{V} = -\frac{\Delta P}{B} + \beta\Delta T \,, \tag{7}$$

where $\beta = 1.2\times10^{-5}K^{-1}$ is the thermal expansion coefficient and $B = 90$ GPa is the volume bulk modulus[2]. To stay with second-order terms with respect to changes in volume and temperature, the $\beta\Delta T$ factor is kept only for the terms of γ and A. Equation 6 therefore becomes

$$\begin{aligned}\frac{\Delta\omega}{\omega} &= \frac{\gamma_0}{B}\Delta P + (A_0 - \gamma_0\beta)\Delta T \\ &\quad + \frac{(g_V - a_T)}{2B}\Delta P\Delta T - \frac{g_T}{2B^2}(\Delta P)^2 \,. \end{aligned} \tag{8}$$

Another observation is that g_V and a_T are mixed partial derivates of the same variables taken in opposite order (and with opposite signs), and therefore must be equal. Then by replacing g_V with a_T, the equation used in the main text is

$$\frac{\Delta\omega}{\omega} = \frac{\gamma_0}{B}\Delta P + (A_0 - \gamma_0\beta)\Delta T - \frac{a_T}{B}\Delta P\Delta T - \frac{g_T}{2B^2}(\Delta P)^2 \,. \tag{9}$$

RAMAN SPECTRA AT 80K

Figure 1 shows four Raman spectra for various pressures at 80 K. At this low temperature, thermal vibrations are suppressed, and the pressure-induced frequency shifts are domi-

* xtong@caltech.edu
† xx2@caltech.edu
‡ btf@caltech.edu
§ hzhang@carnegiescience.edu
¶ tstrobel@carnegiescience.edu
** dkim@carnegiescience.edu

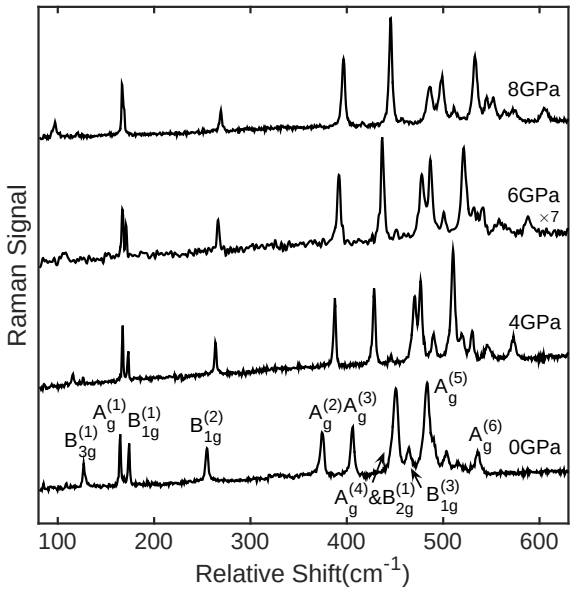

FIG. 1. Raman spectra for pressures of 0, 4, 6, 8 GPa at 80K.

nant. At low frequencies, the interlayer vibrational modes $B_{3g}^{(1)}$ and $B_{1g}^{(1)}$ soften with an increased pressure, due to the negative values of γ and g_T. In contrast, the $A_g^{(1)}$ mode stiffens with pressure, and as a result, the $B_{1g}^{(1)}$ and $A_g^{(1)}$ merge into a single peak at 8 GPa. However, this overlapping is not observed if the temperature is simultaneously increased, as shown in the Raman spectrum of 8 GPa 300 K/400 K in the main text[2]. At higher temperatures the contribution from $\Delta T \Delta P$ competes with the positive Grüneisen parameter for the $A_g^{(1)}$ mode, so the frequency decreases slightly.

At 80K, the Raman peaks at higher frequencies stiffen and spread out with pressure, and overlapped modes like $A_g^{(4)}$ and $B_{2g}^{(1)}$ evolve into distinct peaks. This can be explained by the dominant role of the $[\gamma_0/B]\Delta P$ term in Eq. 9. An increasing, positive value of γ for the high frequency modes ($\omega > 200\,\mathrm{cm}^{-1}$), as listed in Table II in the main text[2], promotes the splitting of these overlapped peaks.

TABLE I. Frequencies for selected Raman peaks in Fig. 1.

Mode	0GPa	4GPa	6GPa	8GPa
$B_{3g}^{(1)}$	127.1	115.7	106.7	96.9
$A_g^{(1)}$	164.7	167.3	167.0	166.9
$B_{1g}^{(1)}$	173.9	173.0	170.9	168.8
$B_{1g}^{(2)}$	254.8	263.7	266.6	269.2
$A_g^{(2)}$	374.5	387.5	391.8	396.5
$A_g^{(3)}$	405.8	428.3	436.9	445.5
$A_g^{(5)}$	483.4	510.2	521.4	533.1
$A_g^{(6)}$	535.8	572.7	588.2	605.4

INFLUENCE OF HELIUM PRESSURE MEDIUM

Given the open-framework nature of Si_{24}, we examined the possibility of whether He atoms could penetrate within the structure and perturb the silicon phonon vibrational frequencies. To test this possibility, we repeated the room-temperature compression experiment using argon as the pressure transmitting medium. For the case of argon, the absolute frequencies and pressure-dependences of the Si_{24} phonons were found to be in quantitative agreement with the case of helium. The only exception was the $B_{3g}^{(1)}$ mode, which was found to exhibit slightly stronger pressure-dependent frequency softening behavior for the argon medium above approximately 2 GPa. We speculate that this difference is caused by subtle differences in non-hydrostatic stress conditions: at 300 K, argon solidifies at 1.4 GPa whereas helium solidifies above 11 GPa. Nevertheless, the reproducibility of all pressure-dependent phonon frequency trends across the two different pressure media confirms that these features are intrinsic to the Si_{24} structure.

[1] Hemley, R., *Ultrahigh-pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, Reviews in Mineralogy, Vol. 37 (Mineralogical Society of America, 1998) pp. 525–559.

[2] Tong, X., Xu, X., Zhang, H., Kim, D., Strobel, T. A., and Fultz, B., *The main paper*.

[3] Wallace, D., *Thermodynamics of Crystals* (Dover, Mineola, N.Y., 1998) pp. 180–186.